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(54) Security Papers

**(57) A security indicator for
incorporation in a printing ink or in**

security paper is a water insoluble
particulate visual indicator precursor
that upon contact with a reducing or
oxidising agent yields a water soluble
visual indicator, such as a dye.

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SPECIFICATION Security Papers

It is known to include in papers various compounds that will give an indication of alteration or forging of value documents printed or written on such papers, such papers being known as security papers. For instance various systems are known for producing a coloured stain in such papers when they are treated with eradicators for aqueous ink, felt tip pen ink, or ballpoint pen ink. Thus it is known to apply a fugitive print of a water soluble ink to the paper so that application of an aqueous eraser results in the print becoming smudged. It is also known to incorporate a material that changes colour upon change of pH. For instance ferrous salts and ferrocyanides may be included in the paper and will give a blue colouration in contact with an acid eraser, or acid-base indicators may be included to give an indication of pH change. Manganese salts may be used to give an indication of the use of oxidising erasers containing hypochlorite. It is also known to include particulate dyes that are soluble in organic solvents, so that they dissolve in contact with an eraser based on an organic solvent and dye the paper.

However, hitherto no entirely satisfactory method has been known to provide a security reaction against reducing agents. Cone (U.S. Patent 1,584,850) has described the use of mercury salts particularly mercurous sulphanilate, to provide protection inter alia against eradication by thiosulphates, sulphites and bisulphites. However such compounds are not particularly sensitive, and moreover they are expensive and unacceptably toxic. Bausch & Schroth (U.S. Patent 2,112,756) describe the use of mercury-tungstate, manganous or barium tellurites, and alkali selenites as indicators for reducing agents. Schroth (U.S. Patent 2,378,585) describes an improved method for using mercury tungstate, barium tellurite or barium selenite as an indicator for reducing agents. All these compounds of mercury, tellurium and selenium are relatively insensitive, expensive and unacceptably toxic.

Organic compounds are not generally suitable as indicators for reducing agents because reduction almost invariably leads to a more saturated product in which the possibility of colour is less than in the starting product. Hence reactions involving reducing reagents rarely lead to an intensification of colour.

The only known practical method of providing security against reducing agents has been to utilise the fact that the most commonly used reducing agents are sulphites or bisulphites which in the first case are alkaline and in the second case become alkaline by loss of sulphur dioxide while drying on the surface of the paper. Accordingly security against sulphite and bisulphite reducing agents can be conferred by incorporating an acid-base indicator in the paper. Such a paper is described by Godet & Bartoli (French Patent 2,365,656) where a number of

known acid-base indicators are described for this purpose. Such a paper suffers from the disadvantage that it only has security against an alkaline reducing agent and the indicator action is readily reversible by means of a weak acid.

The present invention is based on the discovery of a novel type of security indicator. This security indicator can be supplied in security paper or it can initially be supplied in a printing ink suitable for printing onto security paper.

Accordingly a product according to the invention is (1) an ink suitable for use as a printing ink for application to a security paper and which includes a security indicator or (2) a printable paper suitable for use as a security paper and part at least of which is impregnated or coated with a security indicator and the security indicator is a water insoluble particulate visual indicator precursor that, upon contact with a reducing or oxidising agent, yields a water soluble visual indicator.

The visual indicator is generally a true dye and for convenience much of the remainder of the description is written in terms of the use of a dye but instead of being a true dye it may be, for instance, an optical brightening agent or a fluorescent material or any other material that, in the presence of water will give a clear visual indication.

The solid precursor may be a molecular complex formed between an electron donor molecule and an electron acceptor molecule where one of the constituents is a dye molecule or ion and the other is a reducible and/or oxidisable molecule or ion. The precursor may be considered to be a charge transfer complex. Instead of referring to it as a complex it may sometimes be more accurate to refer to it as a salt. It is often preferred that the electron donor should be a water soluble dye and the electron acceptor should be reducible and/or oxidisable.

Many types of reducible and/or oxidisable donor or acceptor are suitable, the only requirement being that it should form an insoluble complex with the dye and should be readily reducible and/or oxidisable to release the dye. Any of the known donor or acceptor molecules may be used provided that they meet the stated requirements. A suitable class of reducible or oxidisable acceptor molecules are the halogen group of elements and particularly iodine. A suitable class of organic donor or acceptor molecules are hydroquinones and quinones and their derivatives. The reducible and/or oxidisable donor or acceptor may itself be a dye, and the complex may be formed between an oxidisable and/or reducible donor dye and a reducible and/or oxidisable acceptor dye.

Many types of dye or other visual indicator are suitable for formation of the complex according to the invention, the essential requirements being that the indicator behaves as an electron donor or acceptor and form an insoluble complex with a reducible and/or oxidisable acceptor or donor molecule and that it should be releasable from

this complex and that, when released, it should be soluble in the medium of the eradicator to form a solution that gives the paper optical properties significantly different from the properties of paper free of the dye.

We have found that many dyes of the diaryl methane, triaryl methane, azo, methine, thiazine, acridine, azine, phthalocyanine, xanthene, thiazole, quinoline and oxazine classes, particularly those having amine or substituted amine groups attached either directly or indirectly to the nucleus, are suitable. The dye may be fluorescent.

Examples of particular complexes that have been found to be very useful in paper according to the invention include the iodine complexes of the following dyes, wherein CI is the Colour Index (3rd edition) published by the Society of Dyers and Colourists and the American Association of Textile Chemists.

CI No.	Dye
21000	Bismarck Brown
41000	Auramine O
42000	Malachite Green
42025	Acronal Brilliant Blue
42040	Brilliant Green
42535	Methyl Violet
44045	Victoria Blue
46000	Acriflavine
46020	Coriophosphine
46025	Acridine Yellow
46040	Euchrysine
47005	Quinoline Yellow
49005	Thioflavine T
50200	Phenosafrine
50240	Safranine O
51175	Iodine Blue
51180	Nile Blue
52030	New Methylene Blue
	CI Basic Blue 33

All of these are new compounds. Other suitable complexes, and which are known from the article by B. Biswas in Chemistry Letters 1975 Pages 177 to 180 published by the Chemical Society of Japan are:

CI No.	Dye
42500	Pararosaniline
42555	Crystal Violet
46005	Acridine Orange
52000	Thionin
52015	Methylene Blue

The new complexes may be made by methods analogous to those described by Biswas.

It is preferable that the complex does not dissociate in or on the paper before contact with eradicator. It may be substantially stable against dissociation within the paper and often it is advantageous to include a low concentration of iodide or other ions in order to suppress any tendency for the complex to dissociate. The iodide or other ions conveniently may be included in the suspension by which the complex is applied to the paper, the iodide ions generally being present in

the suspension in a concentration below 10^{-2} M, generally about 10^{-3} M.

Those complexes formed between the visual indicator and iodine react both to reducing agents and oxidising agents. In the case of reducing agents the iodine of the complex is reduced to iodide ions, releasing the soluble dye. In the case of oxidising agents, the iodine of the complex is oxidised to iodate ion, releasing the soluble dye.

The precursor complex is generally highly coloured. Because it is in particulate form it imparts little or no colouration to the paper, which is thus substantially colourless, but the complexes are generally soluble in organic solvents so that contact of the paper with an eraser based on an organic solvent will, irrespective of whether it is a reducing eraser, generally result in the formation of a coloured stain in the paper.

Some of the complexes dissociate in the presence of acids or alkalis, for instance at pH values below about pH 4 or above about pH 9, to release soluble dye and thus again will form a coloured stain in the paper upon contact with eradicators containing acids or alkalis.

When dissociation of the complex is suppressed by the inclusion of iodide ions in the paper this provides further security against erasure by oxidising agents since they would liberate free iodine by oxidation of the iodide ion where there is sufficient excess of iodide ion and generate a blue or brown stain by reaction of the liberated iodine with starch contained within the paper.

Thus the invention not only permits the presence of a reducing or oxidising eraser to be indicated by a stain or other mark in the paper but the materials used in the invention generally will form a stain or other marks also with erasers based on organic solvents, acids, alkalis or oxidising agents.

Most known systems for providing security against eraser are dependent upon a reaction capable of giving only a single colour. However the method of the invention is not restricted to a single colour but instead a wide range of dyes and thus a wide range of colours can be used. Further the complexes may be used in mixtures, so as to provide still greater variation in possible colours. As examples of the wide ranges in colouration that are obtainable in the invention, the complexes formed between iodine and Methylene Blue, Phenosafranine, Methyl Violet, Bismarck Brown and Auramine O are very satisfactory and yield respectively a blue, red, purple, brown and yellow colour reaction.

The paper that includes the precursor or complex must be suitable for printing in order that it can serve as a security paper, for instance for cheque paper, airline tickets, stock certificates and so forth. The parameters required for the printable papers are well known and generally require that the paper should be sized and should have relatively low porosity. Typically the paper may be both internally and surface sized, have a smooth surface and low porosity. For instance, it

may have a water penetration value as measured by the Cobb test of less than 30, a smoothness as measured by the Bendtsen smoothness tester of less than 200 mls/min at 150 mm's W.G., and an air resistance as measured by the Gurley porosity tester of greater than 12 seconds. In many cases security papers are also required to meet specifications for stiffness and tearing resistance in order that they may be conveniently handled.

For example they may be required to have a minimum stiffness of 0.8 Taber units in the cross direction and 1.5 Taber units in the machine direction, and a minimum tearing resistance of 500 mN in both direction. In some cases they are required to meet a particular specification for substance, caliper, smoothness, stiffness, porosity and tearing resistance such as the CBSI specification (Clearing Banks Specification No. 1) where documents are to be handled on automatic processing equipment.

The amount of the complex in the paper is generally from 0.005% to 0.5% based on the weight of paper, most preferably 0.01 to 0.2%. Per square meter of paper, the amount is generally from 0.005 to 0.5, most preferably 0.01 to 0.2 grams.

The precursor may be applied in a surface coating or it may be present throughout the thickness of the paper. It may be distributed continuously or discontinuously throughout the area of the paper. It may be in a regular pattern or in parts only of the paper. For instance it may be introduced into the paper by conventional methods, for example by inclusion in the pulp from which the paper is made at the wet end of the paper machine, by introduction between the plies of the paper by spraying where the paper is made on a twin wire machine, or by incorporating in a sizing solution that may be impregnated or coated onto the paper during manufacture. Broke containing the complex may be recycled. Alternatively, the complex may be incorporated into a suitable printing ink and applied to the paper in the form of a fugitive background print or any other suitable form of printing, for example a warning phrase or word.

When the security indicator is provided as a printing ink this ink may be formulated in generally known manner.

Although the invention has been described with reference to the stain being formed as a visible indication of an attempt at fraudulent erasure, the application of a reducing or oxidising agent may be conducted in order to authenticate a document.

Many of the complexes described according to the invention are new compounds and form a further part of the invention.

Example

4.5 g of iodine was dissolved in a solution of 20 g of potassium iodide in 500 mls of water. To this solution was slowly added with stirring a solution consisting of 5 g Phenosafranine in 1 litre water. The dye-iodine complex was immediately

formed as a dark reddish brown precipitate. The complex was filtered off and washed with a small quantity of 0.1 M potassium iodide to remove any excess of dye or iodine, and then with water and dried.

1 g of the phenosafranine/iodine complex was dispersed in 500 mls of 10^{-3} M potassium iodide solution using a high speed mixer with an emulsifying head to ensure that the dye was reduced to a fine particulate form. The resulting dispersion was mixed with an equal volume of a 20% solution of an oxidised starch and coated onto the surface of a 96 g/m² sized document paper to give a coating of approximately 2 g/m² when dry. The concentration of the dye complex on the surface of the paper was approximately 20 mg/m² or approximately 0.02% of the weight of the paper.

The paper so obtained was substantially colourless. When treated with an acidic bisulphite solution (pH 5), alkaline sulphite solution (pH 9—10), or acidic stannous chloride solution (pH 4.8), a pink stain developed almost immediately, within 2—3 seconds. When treated with a dilute hypochlorite solution (approximately 0.02% available chlorine) a purple stain developed almost immediately due to the starch iodine reaction.

Example 2

3.6 g potassium iodide was dissolved in 100 mls water, and 5.2 g iodine was added to it. 6.3 g Thioflavine T was dispersed in 200 mls water and added to the potassium iodide and iodine solution. The mixture was stirred for 6 hours, and allowed to stand for a further 20 hours. The solid complex was then filtered off, washed with a little 0.1 M potassium iodide solution, and then with water, and dried.

1.5 g of the Thioflavine/iodine complex was dispersed in 150 mls of water using a high speed mixer fitted with an emulsifying head. 20 mls of the resulting dispersion was mixed with 100 mls of a 20% solution of an oxidised starch and 80 mls of water. The resulting sizing solution was coated onto the surface of a 96 g/m² sized document paper to give a coating of approximately 2 g/m² when dry. The concentration of the dye complex on the surface of the paper was approximately 20 mg/m² or approximately 0.02% of the weight of the paper.

The paper so obtained was substantially colourless. When treated with an acidic bisulphite solution (pH 5), alkaline sulphite solution (pH 9—10), acidic stannous chloride solution (pH 4.8), or dilute hypochlorite solution (approximately 0.02% available chlorine) a yellow stain developed almost immediately.

Claims

1. A product which is (1) an ink suitable for use as a printing ink for application to a security paper and which includes a security indicator or (2) a printable paper suitable for use as a security paper and part at least of which is impregnated or

coated with a security indicator, and in which the security indicator is a water insoluble particulate visual indicator precursor that, upon contact with a reducing or oxidising agent, yields a water soluble visual indicator.

5 2. A product according to claim 1 in which the precursor is a molecular complex or salt formed between an electron donor molecule and an electron acceptor molecule wherein one of the constituents is a molecule or ion of a visual indicator and the other is a reducible and/or oxidisable molecule or ion.

10 3. A product according to claim 1 or claim 2 in which the precursor is highly coloured and is soluble in organic solvent.

15 4. A product according to any preceding claim in which the precursor is a complex or salt between a water soluble visual indicator and a reducible and/or oxidisable electron acceptor.

20 5. A product according to claim 4 in which the

electron acceptor comprises iodine.

25 6. A product according to any preceding claim in which the precursor is a complex of salt of iodine with a dye selected from diaryl methane, triaryl methane, azo, methine, thiazine, acridine, azine, phthalocyanines, xanthene, thiazole, quinoline and oxazine dyes having amine or substituted amine groups attached either directly or indirectly to the nucleus.

30 7. A product according to any preceding claim in the form of a printing ink.

8. A product according to any of claims 1 to 6 in the form of printable security paper.

35 9. A product according to claim 8 in which the paper includes iodide.

10. A product according to claim 8 or claim 9 in which the paper is impregnated or coated uniformly or in a defined pattern with the security indicator.